

Comprehensive assessment of groundwater pollution risk based on HVF model: A case study in Jilin City of northeast China

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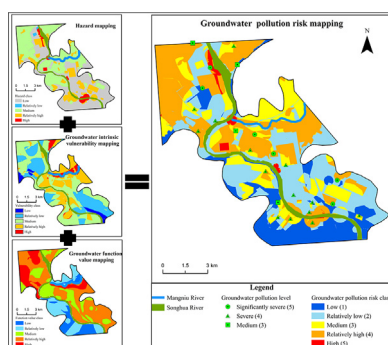
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HIGHLIGHTS

- An HVF model for groundwater pollution risk assessment was proposed.
- The integrated indicator system of groundwater function value was built.
- The model integrated the impact of climate change and human activities.
- Different influence factors lead to relatively high pollution risk in specific areas.
- The correct areas of groundwater pollution risk mapping distribute for 95.81%.

GRAPHICAL ABSTRACT



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ABSTRACT

A comprehensive model for groundwater risk assessment was proposed by combining the hazard of contaminated sources (H), groundwater intrinsic vulnerability (V) and groundwater function value (F), and verified in Jilin City of northeast China. This model is characterized by integrating groundwater resource, ecology, and geological environment under the impact of climate change and human activities. The hazard of potential polluted sources was assessed by quantifying the properties and the potential infiltrating load of contaminants. The groundwater intrinsic vulnerability was evaluated by the DRASTIC model. The groundwater function value was assessed by multiplying seventeen indexes with their corresponding weightings. The groundwater pollution risk mapping of Jilin City was generated based on ArcGIS and validated by the level difference method between the risk classification and the pollution classification. The results showed that groundwater has a relatively low possibility of pollution because the area with less than, or equal to, the medium classification of risk accounted for 67.61% of the study area. The hazard harmfulness from the different contaminant sources played the most important role in determining the high groundwater pollution risk areas. Different influencing factors lead to relatively high pollution risk in specific areas. According to the validation of the level difference method, areas correctly identified by groundwater pollution risk mapping accounted for 95.81% of the study area, which is nearly twice as high as that of specific vulnerability mapping. The HVF model proved to be suitable for assessing groundwater pollution risk in Jilin City of northeast China. The groundwater pollution risk mapping can be applied for the effective protection and sustainable supply of groundwater.

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1. Introduction

Groundwater is a vital water source because about two billion people depend directly upon aquifers for drinking water and 40% of the world's food is produced by irrigated agriculture that relies largely on groundwater (Thiruvengatchari et al., 2008). However, the extensive increases in urbanization, industrialization and climate changes pose risks to the quantity and quality of groundwater (Green et al., 2011; Zhang et al., 2015). Groundwater pollution prevention and control should be given priority in the management of groundwater to avoid costly remediation since groundwater pollution is invisible, complex, and has long-term impacts. Groundwater pollution risk assessment, which refers to the process of determining the potential impacts of any pollutant, is an effective tool for designing efficient groundwater management and protection strategies (Shrestha et al., 2017; Huan et al., 2012).

Studies on groundwater pollution risk assessment have been carried out for >50 years and can be characterized by three main development stages (Zhang et al., 2017). In the first stage, only groundwater vulnerability was regarded as the groundwater pollution risk. In the second stage, various pollution sources were considered jointly with groundwater vulnerability. In the third stage, it has gradually come to an agreement that the risk should be expressed by integrating the probability of contamination occurrence with the expected damage of groundwater system induced by pollution (Baalousha, 2017). The combination of groundwater intrinsic vulnerability and hazard of pollutant sources was often adopted to represent the probability of contaminant occurrence (Nixdorf et al., 2017). Intrinsic vulnerability can be defined as the ease with which a contaminant introduced into the ground surface can reach and diffuse in groundwater under certain geological and hydrogeological conditions (Vrba and Zaporozec, 1994). A hazard is defined as a potential pollutant source at the land surface resulting from human activities (Zwahlen, 2004). The researches of groundwater intrinsic vulnerability were abundant (Pisciotta et al., 2015). The most widely used method for groundwater intrinsic vulnerability evaluation is the DRASTIC model. Existing methods used for the hazard assessment consist of simple judgement, the danger of contamination index, pollutant origin and its surcharge hydraulically (the POSH method), and detailed grading and priority setting (Teng et al., 2012).

Compared with the probability assessment of contamination occurrence, the research on assessment methods for the expected damage of groundwater system is relatively limited. The expected damage can be represented by groundwater function values, which are difficult to estimate because of their highly complex relationships with groundwater pollution risks under the condition of climate change and human activities (Huang et al., 2017; Luoma et al., 2017). A groundwater function value can be classified into an *in situ* value and an *ex situ* (exploitation) value (US-NRC, 1997). The *in situ* value mainly refers to the groundwater function of the aquifer, including sustaining river baseflows, preventing land subsidence, maintaining ecosystem health and preventing aquifer pollution. The *ex situ* value refers to the groundwater function relating to water resource use for domestic, industrial, and agricultural purposes (Zhang et al., 2017). Several indicators of groundwater function value have been proposed, such as water quality and water richness (Zhang et al., 2017), well capture zone (Baalousha, 2011), and specific geological settings (Gemitzi et al., 2006). However, these indicators are lacking of integrated research on building an assessment indicator system of groundwater function value.

A comprehensive model is established to assess groundwater pollution risk accurately by combining the assessments of hazard of contaminants (H), groundwater intrinsic vulnerability (V), and groundwater function value (F) in this work. This model is subsequently referred to as the HVF model. The model considers factors including the climate change, human activities and contamination processes. ArcGIS technique was used to demonstrate the groundwater pollution risk mapping. The HVF model was applied to a case study in Jilin City of

northeast China. The flexibility and effectiveness of HVF model for groundwater management were also investigated.

2. Study area

The study area is approximately 104.5 km² and is located in the floodplain, the first terrace and the second terrace of Jilin City, northeast China (Fig. 1). The Songhua and Mangniu Rivers are the main surface waters. The Songhua River divides the study area into north and south sections. The elevation of the southeastern area is higher than that of the northwestern area. The climate is semi-humid and continental monsoon. The average annual rainfall from 1981 to 2005 was 645.5 mm, and the average annual evaporation was 1506 mm. Holocene alluvium occurs in the floodplain and the first terrace. Upper Pleistocene alluvium occurs in the second terrace. The lower Pleistocene sub-series is continuously overlaid by Holocene alluvium and upper Pleistocene alluvium. The sediments in the vadose zone are mainly loamy sand, sandy loam, sandy clay, loam, silt clay, and silt (EGMSJC, 2008a).

The Songhua River is the main water source and the abundant groundwater resources in the study area serve as important emergency water supplies. The unconsolidated Quaternary deposits, which include sands, gravels, and pebbles, form a significant unconfined aquifer. This aquifer was selected as the target for assessing groundwater pollution risk. The most abundant groundwater resources are found in the floodplain and the first terrace. Recharge takes place mainly by precipitation infiltration and irrigation return from May to August. The groundwater mainly flows to the northwest. Groundwater usually discharges towards the rivers except the flood season. Groundwater exploitation is also an important discharge way, especially in the groundwater source areas of Jiuzhan, Hadawan and Songyuanhada (EGMSJC, 2008a). The study area was divided into 12 subareas according to their geomorphic features and site function divisions.

Groundwater quality has deteriorated gradually in recent years as a result of domestic, industrial, and agricultural pollution. The investigated potential pollutant sources can be classified by shape as the point sources (industry enterprises and domestic sewage outlets), linear sources (polluted open channel at Jiuzhan) and planar sources (fertilizers and pesticides on farmland) (EGMSJC, 2008b).

3. Methodology

3.1. Development of groundwater pollution risk framework

A comprehensive (HVF) model, was proposed to assess groundwater pollution risk by combining the assessment of hazard of contaminants (H), groundwater intrinsic vulnerability (V), and groundwater function value (F). H, V, and F are the ordered categorical variables, which are one type of qualitative variable. Each variable was divided into five classes: low, relatively low, medium, relatively high and high. The ArcGIS-based matrix technique was used to demonstrate the groundwater pollution risk mapping as shown in Table S1. The mappings of H and V were combined to indicate the contamination occurrence probability. Finally, the groundwater pollution risk mapping was generated by overlaying F with the result of the contamination occurrence probability.

3.2. Hazard assessment (H)

The harmfulness of a hazard, i.e. a potential pollutant source, was quantified using Eqs. (1) and (2):

$$HI_j = \sum_{i=1}^n c_{ij} \times Q_{ij} \quad (1)$$

$$C_{ij} = T_{ij}W_T + M_{ij}W_M + D_{ij}W_D \quad (2)$$

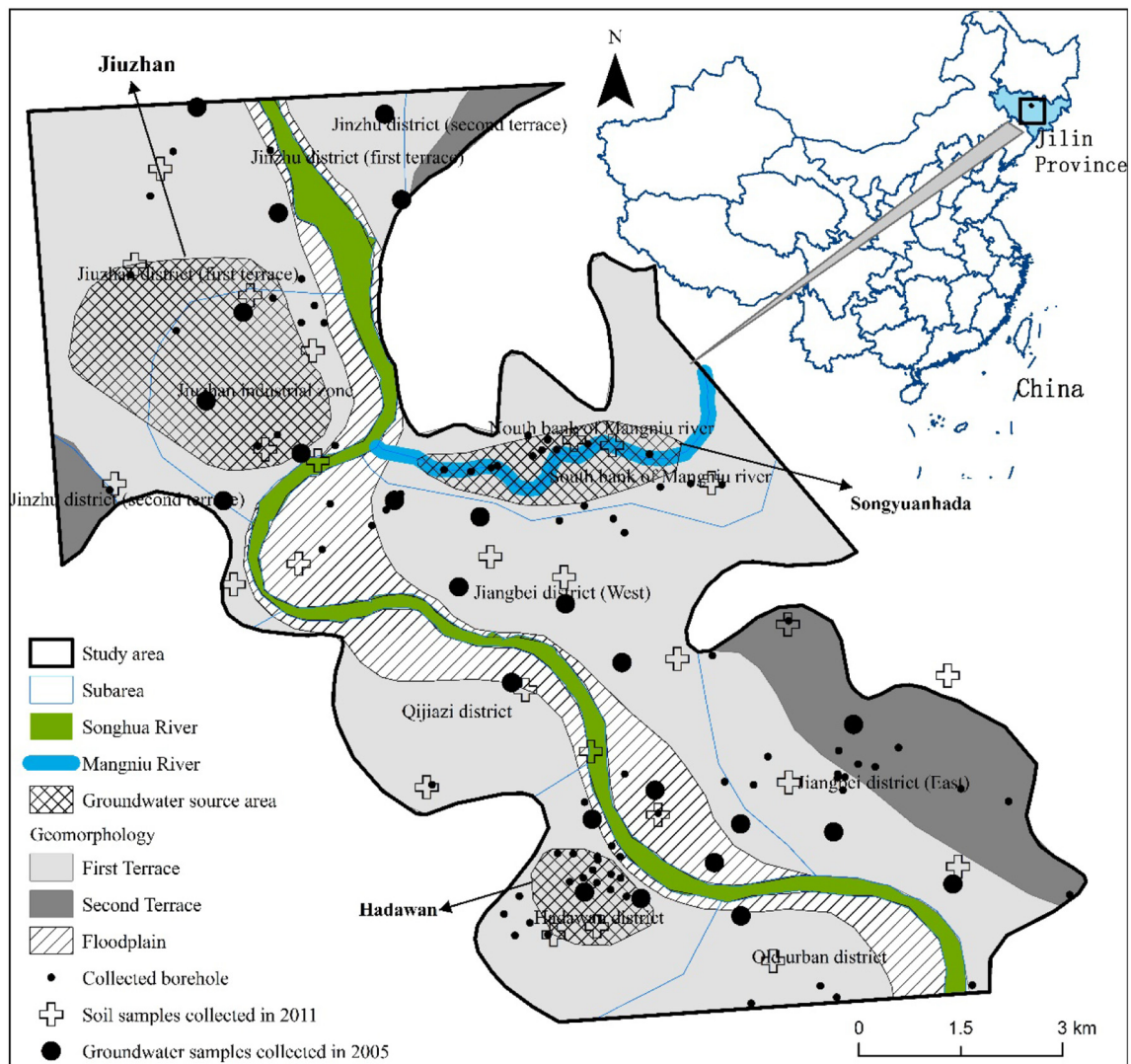


Fig. 1. Location of study area in Jilin City of Jilin Province, China. Jilin Province was marked by blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

where HI_j is the hazard index, which indicates the harmfulness quantification result of the hazard j . There were four types of investigated hazards in the study area: industrial sources, agricultural sources, residential sources and polluted rivers.

C_{ij} is the behavior quantification result of the contaminant i that belongs to hazard j . c_{ij} is the normalized value of C_{ij} . The representative contaminants were selected because they reflect the hazard of contamination characteristics and because they were detected in the groundwater. Representative contaminants were selected from the groundwater sample analysis and the pollutant source investigation results. The selected contaminants included the inorganic compound indicators (SO_4^{2-} , F^- , $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$), heavy metal indicators (Hg, Cr^{6+} , and Zn), and organic compound indicators (benzo[α]pyrene, tetrachloromethane, benzene and volatile phenol) (Table 1). Additionally, total dissolved solids (TDS), chemical oxygen demand (COD), and total hardness (TD) were selected as comprehensive indicators because they can represent unknown contaminants (Wang et al., 2012).

Q_{ij} is the infiltrating contaminant load. This is the evaluated potential quantity of contaminant i from hazard j that can infiltrate the ground. Field investigations, groundwater sampling, background inquiry and data collection were carried out to obtain the values of Q_{ij} from different pollutant sources. These sources included industrial, agricultural and residential sources, and polluted rivers. The assignments of Q_{ij} are

described in Section 1 of the Supplementary material. T_{ij} , M_{ij} , and D_{ij} are the quantified ratings of the properties of contaminant i from hazard j . The toxicity property of representative contaminants was quantified according to the standard for drinking water quality of China (MOH, 2006). Expert analysis was used for quantifying the mobility and degradability of TDS, COD and inorganic contaminants. Table 1 shows the ratings for the three properties of T, M and D. The terms of W_T , W_M and W_D are the corresponding weightings for the toxicity, mobility and degradability properties. Because of the self-healing ability of groundwater and water supply security, it was assumed that the toxicity of a contaminant is more important than its mobility and degradation. Mobility and degradation were assumed to be of equal importance. The Analytical Hierarchy Process (AHP) method was used to determine W_T (0.6), W_M (0.2), and W_D (0.6).

3.3. Groundwater intrinsic vulnerability assessment (V)

The DRASTIC model was used for groundwater intrinsic vulnerability assessment (Alaa et al., 2017; Nobre et al., 2007). The model is composed of seven hydrogeological indexes: Depth to water table (D), net Recharge (R), Aquifer media (A), Soil media (S), Topography (T), Impact of the vadose zone (I), and hydraulic Conductivity (C). Each of these hydrogeological factors is assigned a rating (1–10) and a weighting

Table 1
Groundwater contaminant inventory and the corresponding property rating.

Types	Contaminants	Pollutant sources	Standards ^a (mg/L)	Toxicity rating ^b	IgK _{oc}	Mobility rating ^b	T ₅₀ (d)	Degradability rating ^b	C _{ij}
Comprehensive	TDS	Industry, domestic source	1000	1		14		14	6.2
	COD	Industry, polluted river	5	5		9		1	5.0
	Total hardness	Industry, domestic source, polluted river	450	2		8		10	4.8
Inorganic contaminants	SO ₄ ²⁻	Domestic source, polluted river	250	3		12		11	6.4
	Fluoride	Industry, polluted river	1	6		7		12	7.4
	NH ₄ -N	Industry, agriculture, polluted river	0.5	8		11		2	7.4
	NO ₃ -N	Industry, agriculture, domestic source	20	4		13		3	5.6
Heavy metal	Hg	Industry	0.001	12		6		8	10.0
	Cr	Industry	0.05	9		10		13	10.0
	Zn	Industry	1.00	6		5		9	6.4
Organic contaminants	Benzo[α]pyrene	Industry	0.00001	14	5.95	1	157.87	7	10.0
	Tetrachloromethane	Industry	0.002	11	1.69	4	130.94	6	8.6
	Benzene	Industry	0.01	10	2.22	3	80.35	5	7.6
	Volatile phenol	Industry	0.001	12	2.43	2	30.10	4	8.4

^a Standard for drinking water quality of China (MOH, 2006).^b Refer to the reference (Wang et al., 2012).

(1–5). The DRASTIC index is calculated by applying a linear combination of all the factors according to Eq. (3). The higher the DRASTIC index, the greater the groundwater vulnerability. The data sources and weightings of the DRASTIC indexes can be referred to Table 2. The scores of the seven indexes were set (Table 3) using previous studies (Aller et al., 1987).

$$VI = D_R \times \lambda_D + R_R \times \lambda_R + A_R \times \lambda_A + S_R \times \lambda_S + T_R \times \lambda_T + I_R \times \lambda_I + C_R \times \lambda_C \quad (3)$$

where VI is the groundwater intrinsic vulnerability index. R is the corresponding rating, and λ is the weighting.

3.4. Groundwater function value assessment (F)

The groundwater function value was used to represent potential consequences of a contamination event. The resource function, ecological function, and geological environment function of groundwater were integrated into the assessment of the groundwater function value. An overlay index method involving four major factors of indexes, rating, weighting, and classification was used to assess the groundwater function value. The detailed process of assessing the groundwater function value is described in Section 2 of the Supplementary material.

The resource function value (B1) refers to the role of groundwater supply and is characterized by four attributes: occupancy (C1), regeneration (C2), adjustability (C3), and availability (C4). According to the results of groundwater budget calculation for the study area, precipitation, river runoff and groundwater exploitation were the most important factors influencing the dynamic variation of groundwater. Precipitation and river runoff are affected by climate change, which has impacts on surface water, the control of storage in rivers, and the groundwater recharge process (Earman and Dettinger, 2011; Garner

et al., 2017). The main and direct impact of climate change on groundwater is a change in the volume and distribution of groundwater recharge (Taylor et al., 2013). Groundwater exploitation is influenced by human activity, which can cause groundwater pollution and declination of groundwater levels and storage. The 13 indexes specific to the four attributes embodying the potential impact of climate change and human activity are described in Fig. 2. The ecological function value (B2) refers to the role that the groundwater system has in the maintenance of terrestrial vegetation, lakes, wetlands, and land quality. In general, a larger groundwater depth means less water content in the soil and a lower quality ecological environment (Xu et al., 2007). Therefore, the soil type and groundwater depth were selected as the indicators of the ecological function value of the groundwater system. They are graded and assigned based on the results of a groundwater ecological function evaluation in the same study area (Fan, 2007) (Table S2). The geological function value (B3) refers to the role that the groundwater system plays in the stability of its geological environment. B3 is represented by the cone of depression and the ratio between the variation in recharge rate and water level. In summary, four layers (system layer A, function layer B, attribute layer C and index layer D) and 17 indexes were used to characterize the groundwater function value (Fig. 2). Detailed explanations and data sources for the groundwater function value determination are described in Table S3.

The index for the groundwater cone of depression (D16) was set as 0.99 for the areas with a cone of groundwater depression, and 0.01 in areas without a cone of groundwater depression. Using the standard of groundwater quality (GB/T 14848 - 93) of China, the index of groundwater quality (D12) was classified into five grades (I, II, III, IV, and V) with corresponding assignment of 0.99, 0.75, 0.50, 0.25, and 0.01. The ratings for the ecological function indexes are shown in Table S3.

The index importance of Layer B was determined by expert analysis, and was graded from high to low according to the following sequence:

Table 2
Data used for the creation of the seven parameter data layers of DRASTIC model.

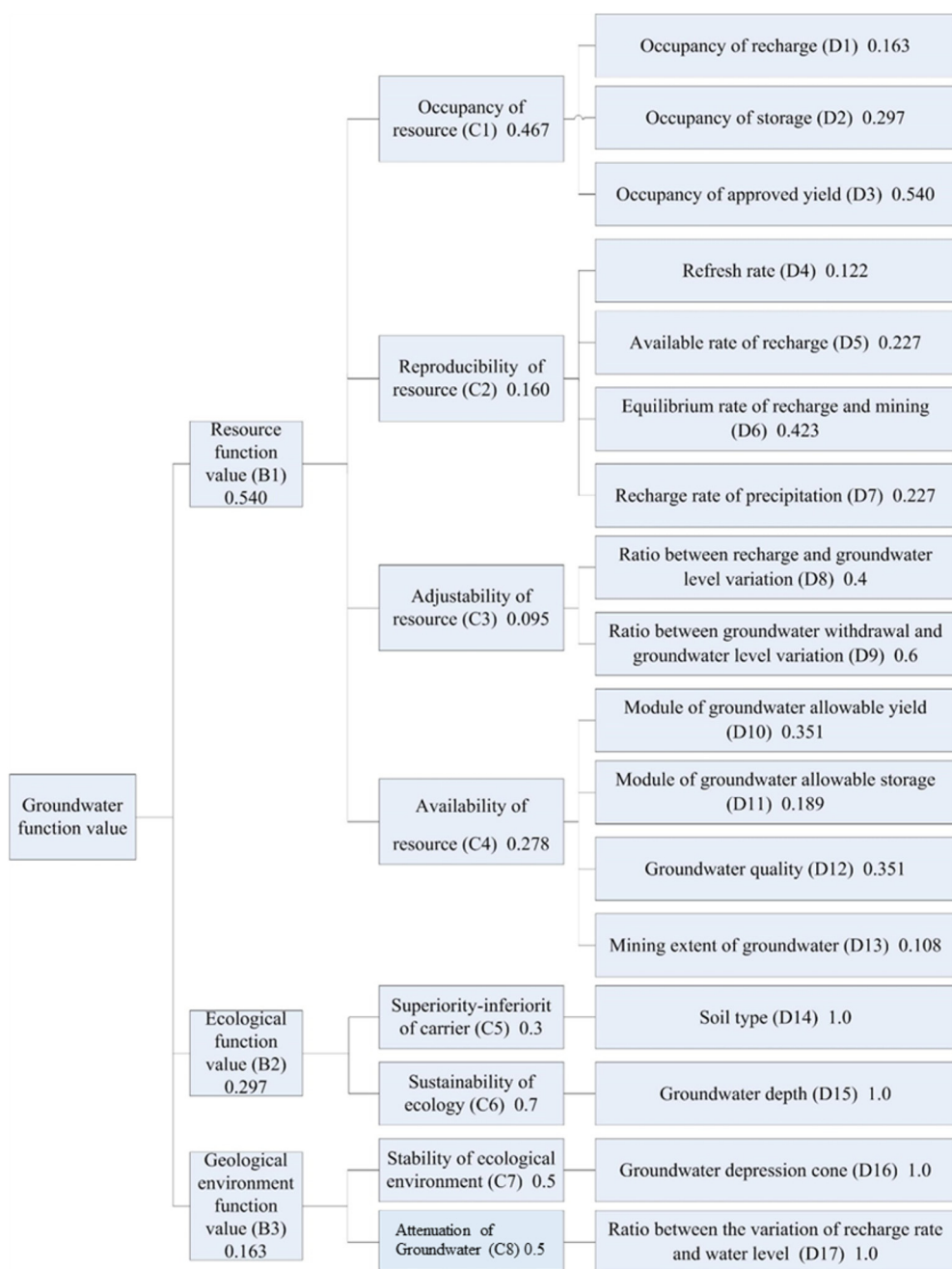
Index	Parameter definition	Weighting ^b	Data source
D	Depth to groundwater	5	34 monitoring wells
R	Net recharge	4	Precipitation and irrigation data
A	Aquifer media	3	84 drilling bar charts
S	Soil type	2	28 particle size analysis of soil samples
T	Topography	1	84 drilling bar charts
I	Impact of vadose zone	5	84 drilling bar charts
C	Hydraulic conductivity	3	Hydrogeology survey report and groundwater dynamic monitoring report of Jilin City ^a

^a EGMSJC (2008a, 1997, 2002).^b Refer to the reference (Aller et al., 1987).

Table 3

Score criteria of the DRASTIC method indexes for the groundwater vulnerability assessment.

D (m)	R (mm/a)	A	S	T (%)	I	C (m/d)	Scores
≤2	>254	Gravel	Thin or absent	≤2	Gravel	>81.5	10
(2,4]	(235,254]	Sand and gravel	Cobble and gravel	(2,4]	Sand and gravel	(61,81.5]	9
(4,6]	(216,235]	Coarse sand	Gravel, medium or coarse sand	(4,7]	Coarse sand	(40.7,61]	8
(6,8]	(178,216]	Medium sand	Silt or fine sand	(7,9]	Medium sand	(34.6,40.7]	7
(8,10]	(148,178]	Sand	Shrinking or aggregating clay	(9,11]	Sand	(28.5,34.6]	6
(10,15]	(117,148]	Fine sand	Sandy loamy	(11,13]	Fine sand	(20.3,28.5]	5
(15,20]	(92,117]	Silty sand	Loam	(13,15]	Silty sand	(12.2,20.3]	4
(20,25]	(71,92]	Sandy loam	Silty loam	(15,17]	Sandy loam	(8.1,12.2]	3
(25,30]	(51,71]	Silty clay	Clayey loam	(17,18]	Silty clay	(4.1,8.1]	2
>30	(0,51]	Clay	Non-shrinking or non-aggregated clay	>18	Clay	≤4.1	1

**Fig. 2.** Hierarchical index system of groundwater function value. The number after the parentheses represents the weighting of index. C1–4 are affected by the climate change and human activities.

resource > ecological > geological environmental. In the resource function value assessment, it was believed that the importance of occupancy was highest, followed by availability, reproducibility, and adjustability. A similar analysis of index importance was conducted for layer D. The index weightings in different layers (B, C, and D) were subsequently estimated by the AHP method (Fig. 2). Distribution of the 17 index layers representing the groundwater function value were obtained using ArcGIS.

The comprehensive index for groundwater function value (FI) was obtained using Eqs. (4)–(8). The higher the number of FI value, the higher the groundwater function value.

$$FI = B_1W_1 + B_2W_2 + B_3W_3 \quad (4)$$

$$B_1 = \sum_{j=1}^4 m_j C_j \quad (5)$$

$$B_2 = \sum_{j=5}^2 m_j C_j \quad (6)$$

$$B_3 = \sum_{j=7}^8 m_j C_j \quad (7)$$

$$C_j = \sum_{i=1}^I n_i D_i \quad (8)$$

where B_1 is the resource function value, B_2 is the ecological function value, and B_3 is the geological environment function value. W_1 , W_2 , and W_3 are weightings of B_1 , B_2 , and B_3 . The terms m_j and n_i are weightings of index j in layer C and index i in layer D, respectively. C_j and D_i are ratings of index j and i , respectively. B_1 , B_2 , B_3 and A are classified into five ranks as Table 4 shows.

3.5. Validation of groundwater pollution risk mapping

The reliability of groundwater pollution risk assessment results was tested using the level difference method between the groundwater pollution risk classification and the groundwater pollution classification. The method of groundwater pollution assessment is described in Section 3 of the Supplementary material. The assessment results for groundwater pollution and groundwater pollution risk were divided into the same number of levels. Groundwater pollution was classified

into five levels: none, slight, medium, severe, and significantly severe, which were represented by levels of 1, 2, 3, 4, and 5 respectively. Groundwater pollution risk was also divided into five levels: low, relatively low, medium, relatively high, high, which were represented by levels of 1, 2, 3, 4, and 5 respectively. The level difference was obtained by calculating the absolute difference value of the two variables. The pollution risk assessment was considered correct when the level difference was -1 through to 1 . The pollution risk was considered underestimated or overestimated when the absolute value of the level difference was 2 or 3, and extremely underestimated or overestimated when the absolute value of the level difference was 4 (Stigter et al., 2006).

3.6. Sensitivity analysis

Sensitivity analysis provides helpful information on the influence of rating and weighting values assigned to each index and assists the analyst in judging the significance of subjective elements. A single-parameter sensitivity analysis was used to evaluate the impact of each factor on the assessment result as follows (Insaf and Mohamed, 2005):

$$W = (P_r P_w / R) \times 100 \quad (9)$$

where W is the effective weighting of each parameter, P_r and P_w are rating and weighting values of each parameter, respectively, and R is the index of the assessment result.

4. Results and discussion

4.1. Hazard mapping

C_{ij} was calculated according to Eq. (2). The ratings of the three properties and C_{ij} values of each contaminant are demonstrated in Table 1. Industrial contaminant sources were deduced to discharge all of the representative contaminants except SO_4^{2-} , into the groundwater. Nitrate, COD, volatile phenol, ammonium, total hardness, and TDS were identified from residential sources with concentrations of 25.60 mg/L, 5965.70 mg/L, 1.90 mg/L, 2086.25 mg/L, 613.00 mg/L, and 1275.00 mg/L, respectively. Ammonium, sulfate, fluoride, volatile phenol, COD, and total hardness were confirmed to be specific contaminants of the polluted river with concentrations of 8.78 mg/L, 401.00 mg/L, 1.16 mg/L, 0.004 mg/L, 39.60 mg/L, and 889.00 mg/L, respectively (EGMSJC, 2008b). Values for Q_{ij} from the industrial sources,

Table 4
Ratings and significance for groundwater function value.

Functions and codes	Rating	State level	Functional status	Prospect
Resource function value (B1)	>0.84	I	High	Large-scale exploitation
	(0.67, 0.84]	II	Relatively high	Moderate exploitation
	(0.34, 0.67]	III	Medium	Regulated exploitation
	(0.17, 0.34]	IV	Relatively low	Careful exploitation
	≤0.17	V	Low	Restricted exploitation
Ecological function value (B2)	>0.84	I	High	Large-scale utilization
	(0.67, 0.84]	II	Relatively high	Moderate utilization
	(0.34, 0.67]	III	Medium	Regulated utilization
	(0.17, 0.34]	IV	Relatively low	Careful utilization
	≤0.17	V	Low	Restricted utilization
Geological function value (B3)	>0.84	I	High	Protection
	(0.67, 0.84]	II	Relatively high	Conservation
	(0.34, 0.67]	III	Medium	Utilization
	(0.17, 0.34]	IV	Relatively low	Dilution
	≤0.17	V	Low	Weakening
Groundwater function value	>0.8	I	High	Strong groundwater sustainability, high expected damage
	(0.6, 0.8]	II	Relatively high	Relatively strong groundwater sustainability, relative high expected damage
	(0.4, 0.6]	III	Medium	Moderate groundwater sustainability, medium expected damage
	(0.2, 0.4]	IV	Relatively low	Relatively weak groundwater sustainability, relatively low expected damage
	≤0.2	V	Low	Weak groundwater sustainability, low expected damage

agricultural sources, residential sources and polluted rivers were determined according to Eqs. (S1)–(S4).

After the assignment of Q_{ij} , the hazards from industrial sites, drain outlets, agricultural areas, rural residential areas and polluted river were assessed using Eq. (1) and illustrated as Fig. 3 by the spatial analysis of ArcGIS. It was calculated that the agricultural HI was between 0 and 0.060, industrial HI ranged between 0 and 16.565, rural residential HI was between 0 and 1.400, and the polluted river HI was 1.96. The composite HI_j in the study area was 0–17.156, and it was divided into five classes according to the quantile method: low [0, 0.055), relatively low [0.055, 0.198), medium [0.198, 0.652), relatively high [0.652, 1.960), and high [1.960, 17.156].

As Fig. 3 shows, low and relatively low potential harmfulness classes dominate the study area (80.98%), which were mainly affected by agricultural sources. The medium potential harmfulness class accounts for 7.23% of the study area, and is found sporadically at the specific industrial sites (chemical fertilizer plant, Jilin cement factory, chemical fiber mill, and sugar factory) and rural residential areas located in the Jiangbei District. The area with a relatively high potential harmfulness class accounts for 8.14% of the study area and is associated with the hazards of the polluted river, specific industry sites (phenol-acetone plant, thermal power plant, carbon factory, ferroalloy factory, and Jidong cement

plant) and the rural residential areas located in the Qijiaz District, Jiuzhan District, and along the Mangniu River. The high potential harmfulness class occupies only 3.65% of the study area, and is associated with the polluted river, 11 industrial discharge outlets, and a few industrial sites (paper mill and sewage treatment plant of Jilin chemistry).

4.2. Groundwater intrinsic vulnerability mapping

Groundwater intrinsic vulnerability mapping (Fig. 4) was generated using the DRASTIC model (Eq. (3)) and ArcGIS. The calculated value of VI ranged from 98 to 174, and it was divided into five classes of vulnerability according to the equal interval method: low, relatively low, medium, relatively high, and high. From the statistics of the single-parameter sensitivity analysis for the intrinsic vulnerability (Table 5), the effective weighting was between 5.22% and 23.42%, indicating that the five indexes in the vulnerability assessment show obvious difference. The groundwater depth exhibited the highest effective weight, followed by the impact of vadose zone, net recharge, hydraulic conductivity, and aquifer media. In comparison, soil type and topography exerted little influence on the vulnerability distribution. The significance of groundwater depth, impact of vadose zone, net recharge, and

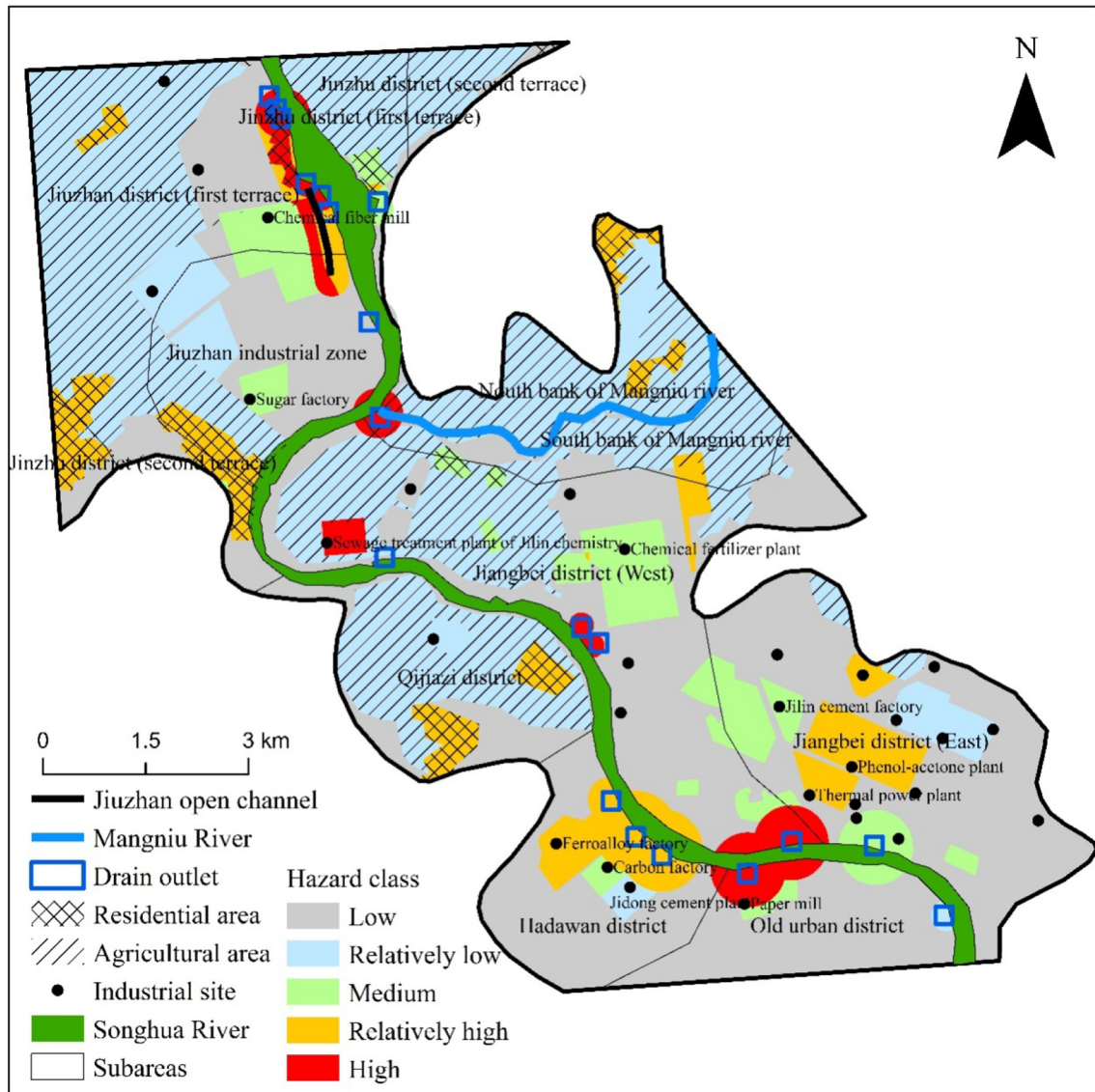


Fig. 3. Hazards mapping of the study area.

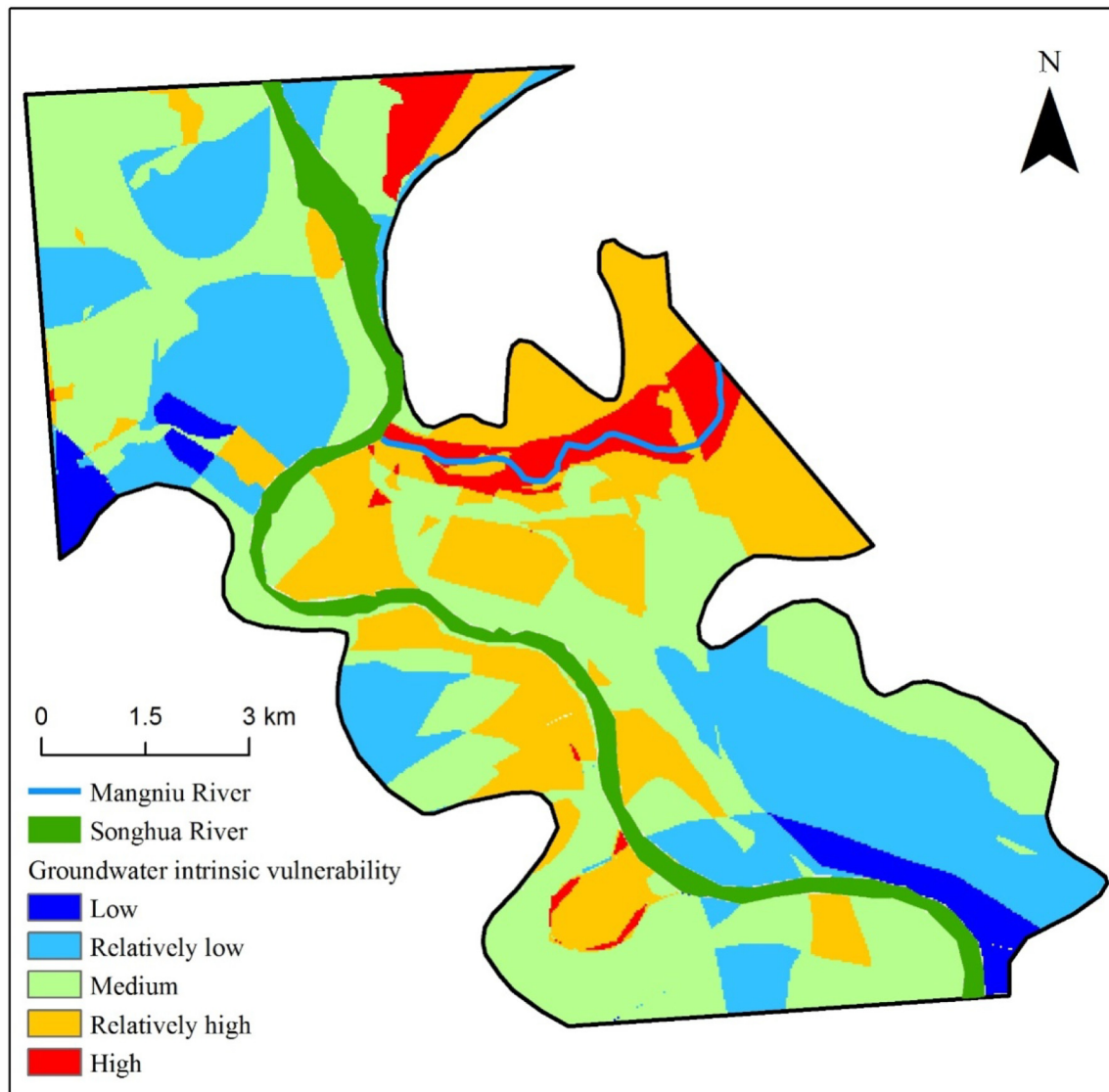


Fig. 4. Groundwater intrinsic vulnerability mapping assessed by DRASTIC model.

hydraulic conductivity highlights the importance of obtaining accurate, detailed, and representative information for these factors.

The high groundwater vulnerability areas are mainly located in the floodplain of the Mangniu River, partly in the first terrace, and are largely controlled by the vadose zone and net recharge. The vadose zone is mainly composed of sandy loam or loamy sand, and thus high net recharge may carry large amounts of contaminants from the surface to the groundwater. The relatively high vulnerability areas are located contiguously in the floodplain of the Songhua River and first terrace of the Mangniu River. The vadose zone in the relatively high vulnerability areas is primarily silt loam or sandy loam which can retard the

downward migration of contaminants into the aquifer. The vadose zone type, and net recharge and hydraulic conductivity are responsible for the extent of the relatively high vulnerability distribution. Areas of low and relatively low vulnerability are largely concentrated in the second terrace and the back of the first terrace. The possibility of groundwater pollution was reduced by the deep groundwater table, the ability of silty loam in the vadose zone to retard infiltration, and the small amount of net recharge.

4.3. Groundwater function value mapping

The comprehensive index of groundwater function value (FI) was calculated using Eqs. (4)–(8) and classified as shown in Fig. 5. It can be seen (Fig. 5) that 12.88% of the study area has a high function value in the first terrace of Jiuzhan District and in the south bank of the Mangniu River. The groundwater function value in the Jiuzhan District is controlled by the resource function value, followed by the geological environment function value and the ecological function value. The high function value in the north of Jiuzhan District is caused by the occurrence of a groundwater cone of depression, relatively high occupancy, and availability of the resource. The groundwater function value in the south bank of the Mangniu River is dominated by occupancy and availability of the resource function value because the

Table 5
Statistics of the effective weightings of groundwater intrinsic vulnerability indexes.

Index	Effective weighting (%)			
	Min	Max	Average	Standard deviation
Depth to groundwater	14.4	51.02	23.42	5.23
Net recharge	6.58	25.36	15.63	7.32
Aquifer media	15.22	26.11	13.04	0.05
Soil type	4.08	12.36	7.66	5.16
Topography	2.19	13.04	5.22	0.56
Impact of vadose zone	11.95	35.91	19.78	2.13
Hydraulic conductivity	13.62	25.48	15.26	6.52

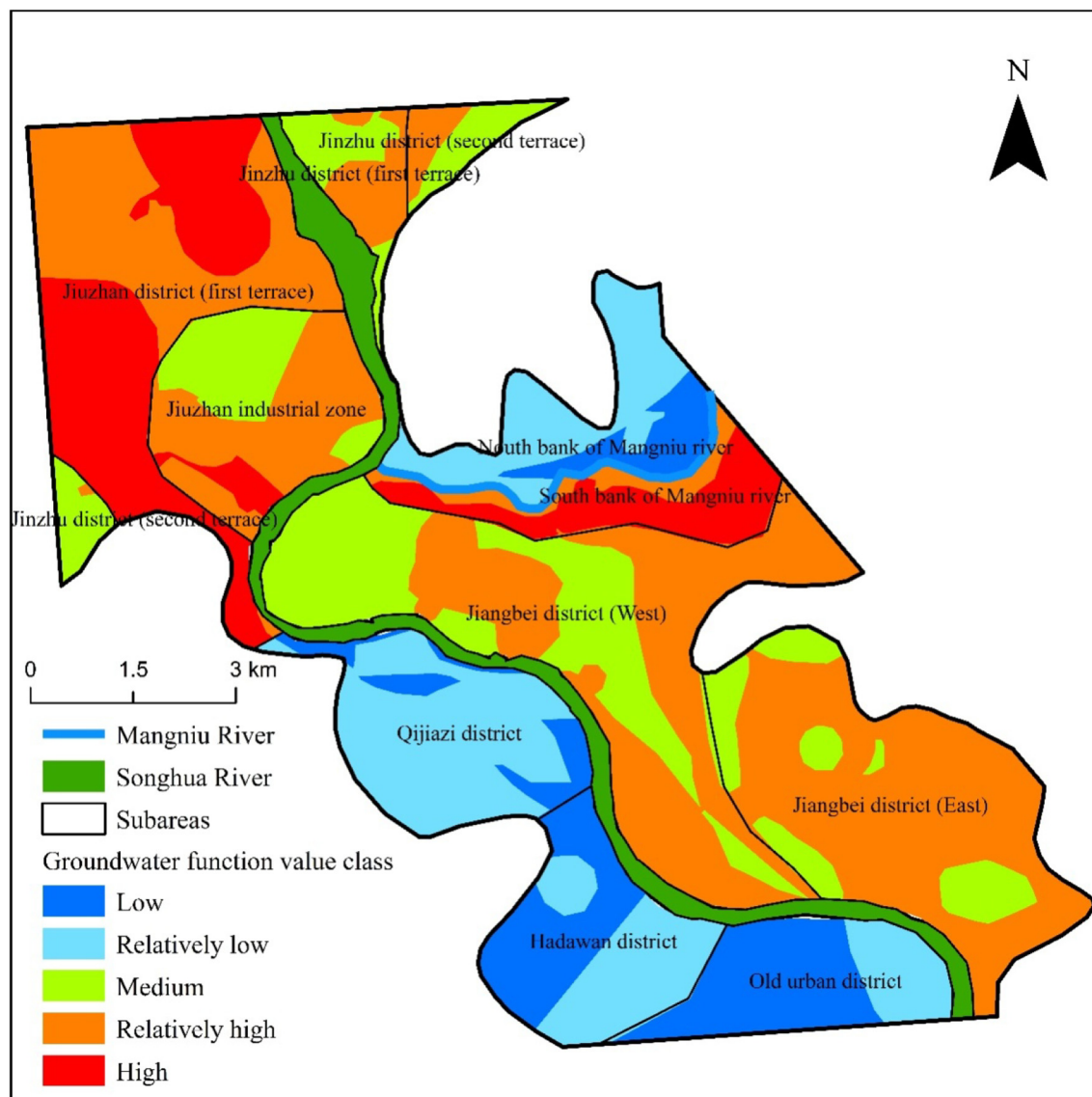


Fig. 5. Groundwater function value mapping of the study area.

groundwater source area of Songyuanhada is abundant in storage, mining extent and recharge of groundwater. Groundwater with a relatively high function value is widely distributed (40.95% of the study area) in the Jiuzhan industrial zone, the first terrace of Jiuzhan and Jinzhu Districts, and most of the Jiangbei District. The areas are dominated by occupancy and availability for resource function values, and by soil type for the ecological environment function value. Medium class groundwater function values are mainly found in the Jiuzhan industrial zone, the Jinzhu District and parts of the Jiangbei District. Groundwater has medium resource function values, which are the results of medium/relatively low function values for the ecological and geological environment. The index importance in the medium class of groundwater function is determined from high to low by the following sequence: geological function > ecological function > resource function. In comparison, the north bank of the Mangniu River, the Qijiazi and Hadawan Districts, and the old urban district have relatively low and low groundwater function values, which occupy 17.19% and 10.89%, respectively, of the study area. On the whole, the ecological and geological function values outweigh the resource function and the expected damage of groundwater pollution is low.

The average effective weightings for each index in layers B, C, and D for the groundwater function value are shown as Fig. 6. The resource function value (B1) dominates the groundwater function value in the study area, with an average effective weighting of 53.58%. The next highest values affecting the groundwater function value are the ecological function value (B2) (30.11%) and the geological environment value (B3) (16.32%). For the layer C, the indexes that mainly control the groundwater function value are the occupancy of resource (C1), sustainability of ecology (C6), and availability of resource (C4). These indexes have an average effective weighting of >15%. For the layer D, the groundwater depth (D15) plays the most important role in the groundwater function value (20.79%) followed by the occupancy of approved yield (D3) (13.62%). In addition, the groundwater function value is also affected by the soil type (D14), groundwater depression cone (D16), the ratio between the variation of recharge rate and groundwater level (D17), occupancy of storage (D2) and module of groundwater allowable yield (D10). The average effective weightings of these indexes are between 5% and 10%.

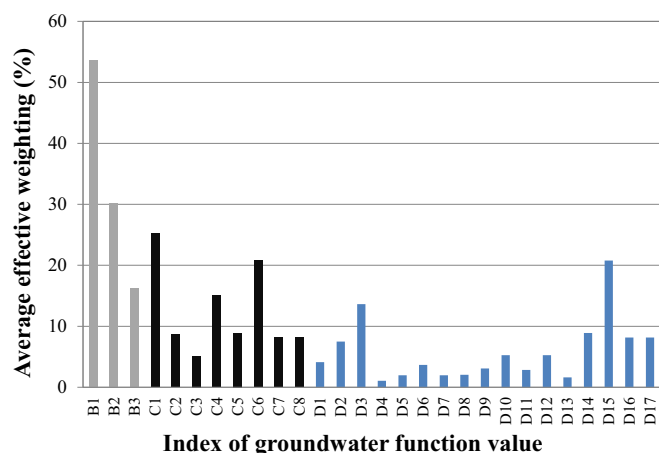


Fig. 6. Average effective weightings of each index on the groundwater function value. The grey pillars represent the results of B1, B2 and B3 on the function value. The black pillars represent the results of C1–C8 on the function value. The blue pillars represent the results of D1–D17 on the function value. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.4. Groundwater pollution risk mapping

The groundwater pollution risk mapping (Fig. 7) was generated by spatially overlaying of the intrinsic vulnerability mapping, hazard mapping and groundwater function value mapping using ArcGIS. The high groundwater pollution risk area occupies only 2.18% of the study area. This area is sporadically distributed in the vicinity of the polluted river, an industrial site (sewage treatment plant of Jilin chemistry) and discharges from a chemical plant and a chemical fiber factory. The relatively high groundwater pollution risk areas, which account for 30.31% of the study area, are distributed continuously in the floodplain, the first terrace, and part of the second terrace of the Songhua and Mangniu Rivers. The total areas of low and relatively low pollution risk are distributed throughout nearly half of the study area, and are specifically found in the Jiuzhan industrial zone, the Qijiazhi, Jiangbei District, and Hadawan Districts and the old urban district.

The groundwater pollution risk mapping illustrated that the groundwater in the study area has a relatively low possibility of contamination because the areas with less than, or equal to, the medium risk classification accounted for 67.61% of the total area. The most important factors in the high groundwater pollution risk areas were hazard harmfulness from point sources (drain outlets), line source (Jiuzhan open channel),

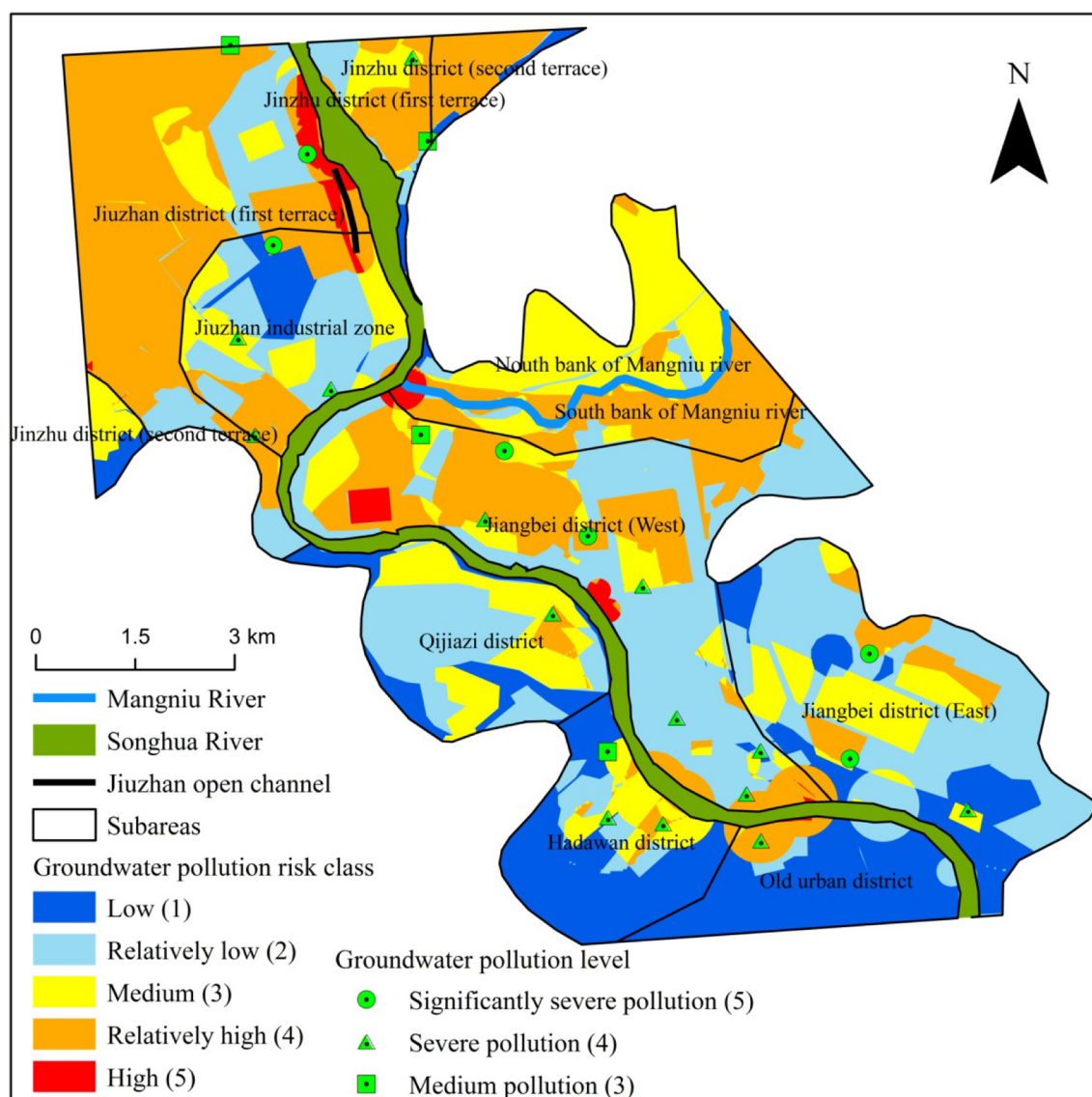


Fig. 7. Groundwater pollution risk mapping of the study area.

and planar sources from industrial sites. The second most important factors were the relatively high groundwater function value and the relatively high groundwater intrinsic vulnerability. Diverse factors lead to relatively high pollution risks in specific areas. Specifically, the groundwater function value dominated the classification in the area of the first terrace of Jiuzhan district, Jinzhu district and the south bank of the Mangniu River. In these areas, the resource function value was controlled by reproducibility and regulatory of resource. Groundwater exploitation and climate change exert a key influence on the distribution of relatively high pollution risk in the above areas. The groundwater intrinsic vulnerability is the key factor of relatively high risk areas in the Qijiazi District, west of Jiangbei District and the second terrace of Jinzhu district. In these relatively high risk areas, effective and sustainable groundwater exploitation strategies can, at least, maintain the groundwater current function value, and prohibit new contaminant sources and reduce pollutant loading. The hazard harmfulness from some industrial discharge outlets along the Songhua River affects the distribution of the relatively high pollution risk. The effective measures are needed to reduce the discharge on the emission reduction of industrial wastewater and meeting the discharge standards for of the industrial waste, and thus reduce sewage should be taken to effectively bring down the groundwater pollution risk. In the most areas with a low or

relatively low pollution risk, the controlling factor is groundwater intrinsic vulnerability except the Jiangbei District, which is dominated by hazard of contaminant sources hazard. The natural conditions in the vadose zone and the aquifer effectively protect the groundwater from pollution. Therefore, restricting new contaminant sources is the key to maintaining the low groundwater pollution risk in the above areas.

The accuracy of the groundwater pollution risk mapping is closely related to the different grading methods used for vulnerability, hazard, and function values. The grading methods are generally determined by the data characteristics, and can be revised according to the validation results of the risk mapping.

4.5. Validation of groundwater pollution risk mapping

According to the groundwater pollution assessment presented in the supplementary material, there are three levels of groundwater pollution in the study area: medium pollution (3), severe pollution (4) and significantly severe pollution (5). There are no levels of non-pollution (1) and slightly severe pollution (2) (Fig. 7). The spatial distribution of each level difference was obtained by the inverse distance weighted interpolation method based on the absolute value of level difference at the 24 sampling sites in the spatial analysis module of ArcGIS (Fig. 8). The area

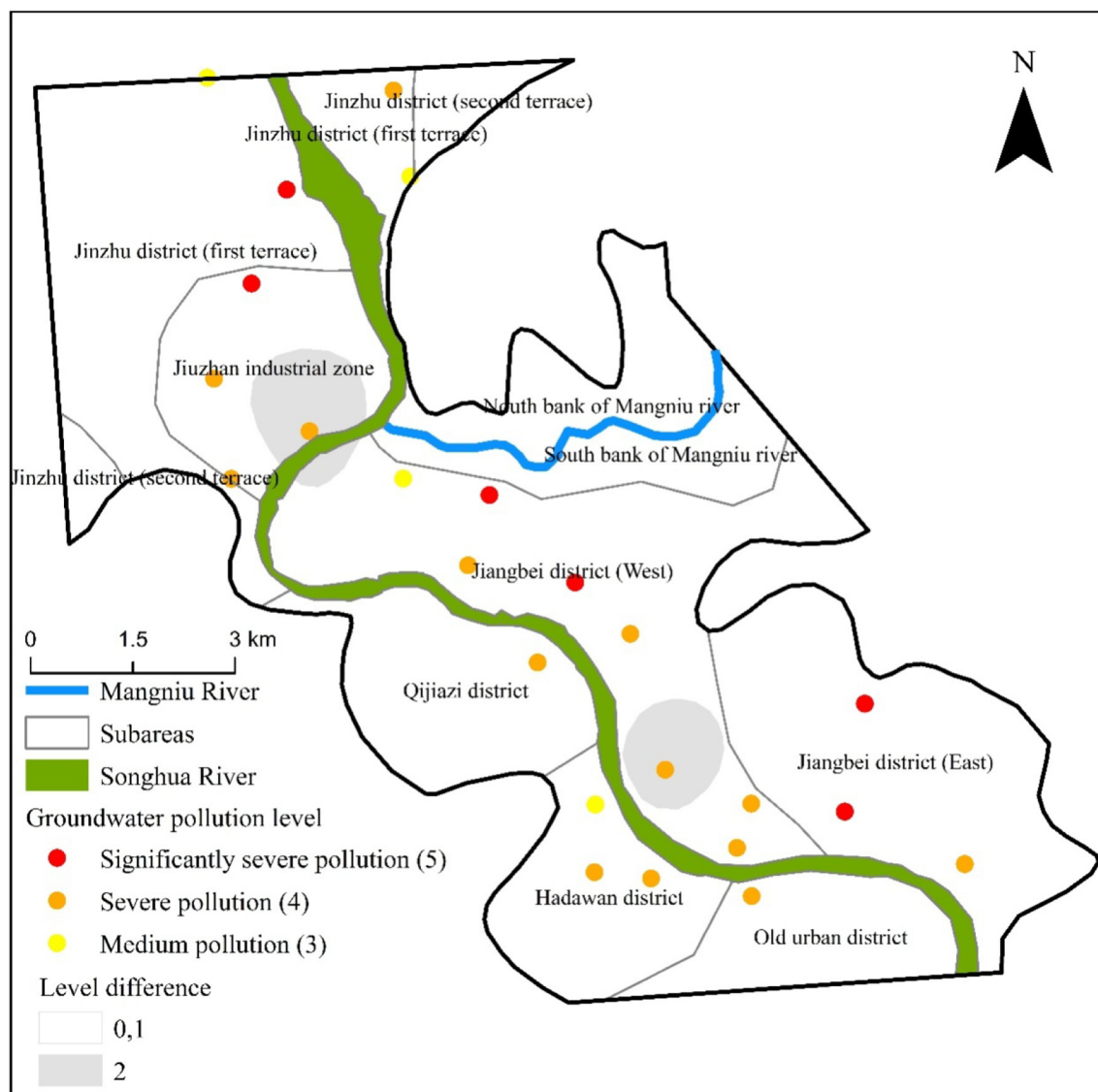


Fig. 8. Distribution of level difference between the groundwater pollution risk classification and groundwater pollution classification.

percentage for level differences that correctly assessed areas of groundwater pollution risk mapping was 95.81%. The underestimated pollution risk areas account for 4.19% of the study area. Thus, the proposed method proved to be effective for the study area. Underestimated pollution risk areas are located in the Jiuzhan industrial zone and the Jiangbei District. In these areas, severe pollution corresponds to relatively low groundwater pollution risk. The hazard harmfulness exerts the most effect on the distribution of relatively low pollution risk. According to the groundwater pollution assessment, groundwater pollution in the underestimated pollution risk area is affected by high levels of Cl^- , SO_4^{2-} , $\text{NO}_3\text{-N}$, TDS, and TD. These high levels are inferred to have originated from rural residential sewage and fertilizers. The accuracy of the groundwater pollution risk could be improved if there are further investigations of agricultural and domestic pollution sources. Moreover, there is not enough validation in the low and relatively low pollution risk areas because of a limited number of groundwater sampling points. The sampling points were mainly distributed in the polluted areas. It is suggested that more representative groundwater sampling should be carried out for further validation of the HVF model.

It is important to check the accuracy of the groundwater pollution risk mapping. The choice of appropriate validation criteria is still disputed in the literature. The level difference method is characterized by regional validation instead of being limited to a few sample locations. The level difference method assumes that groundwater pollution result is in direct proportion to the groundwater pollution risk. Its advantages are that it is easy to use, has a wide application, has low data requirements, and provides a clear explanation of the validation. The disadvantages of this method are the uncertainty of validation results because of the different classification methods used in the groundwater pollution and pollution risk assessments.

Huan et al. (2012) assessed the specific vulnerability to nitrate by using a modified DRASTIC model, and adopted the level difference method to validate the results in the same study area. The statistical analysis of level differences showed that the area of correct vulnerability assessment accounted for 64.45% of the study area (Huan et al., 2012), which was almost 33% lower than that area percentage of correct pollution risk assessment. In addition, the Spearman correlation coefficient for specific vulnerability and nitrate data was 0.6698 (Huan et al., 2012), which was 0.2327 lower than the correlation coefficient between pollution risk and groundwater quality. Therefore, it can be noticed that the positive correlation between groundwater pollution risk and groundwater quality is higher than the correlation between specific vulnerability and quality data. The key distinction between the assessment of specific vulnerability and pollution risk originates from the hazard of potential polluted sources (Nixdorf et al., 2017) and groundwater function value (Zhang et al., 2017).

5. Conclusions

The comprehensive HVF model was successfully established to assess the groundwater pollution risk for Jilin City by combining the hazard of pollutant sources, groundwater intrinsic vulnerability, and groundwater function value. The assessment of groundwater function value integrated indicator systems for the effects of climate change and human activity. The groundwater of Jilin City has a relatively low possibility of contamination because the areas with a less than, or equal to, medium classification risk accounted for 67.61% of the study area. The high groundwater pollution risk areas were mainly controlled by the integrated hazard harmfulness from the different contaminant sources. The relatively high pollution risk areas had different influencing factors. Correct areas of groundwater pollution risk mapping accounted for 95.81% of the study area. The HVF model was proved to be suitable for assessing groundwater pollution risk at a regional scale. It can provide effective support to the groundwater management because of its flexibility and clear explanation of the results.

The accuracy of the groundwater pollution risk could be improved if there is further investigation of agricultural and domestic pollution sources. More representative groundwater samplings could be collected in the low and relatively low pollution risk areas for further validation of the HVF model.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.02.130>.

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